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IT

79-31-2

(lithiation-alkylation of)

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COMMAND STACK INTERRUPTED.
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TO SEE WHICH COMMANDS WERE EXECUTED.
=> d acc all 102:095383p
ANSWER 1
         COPYRIGHT 1992 ACS
     CA102(11):95383p
AN
     Phenethanolamine derivatives useful in the treatment of respiratory
TΤ
    problems
     Skidmore, Ian Frederick; Lunts, Lawrence Henry Charles; Finch,
AU
     Harry; Naylor, Alan
CS
     Glaxo Group Ltd.
LO
     UK
SO
     Ger. Offen., 82 pp.
PΙ
    DE 3414752 A1 18 Oct 1984
    DE 84-3414752 18 Apr 1984
AΙ
PRAI GB 83-10477 18 Apr 1983
    GB 83-17087 23 Jun 1983
     GB 83-29568 4 Nov 1983
     GB 84-1889 25 Jan 1984
IC
     C07C093-08; C07D317-54; C07D319-18; A61K031-135
     25-10 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)
SC
SX
     63
DT
     P
CO
    GWXXBX
PΥ
     1984
     Ger
LA
     Diagram(s) available in offline prints and/or printed CA Issue.
GI
     Title compds. (I) (m = 2-8; n = 1-7; Ar = aryl, R, R1 = H, C1-3)
AB `
     alkyl) were prepd. as .beta.-adrenoreceptor stimulants (no data).
     Thus 4,3-(HO)(HOCH2)C6H3CH(OH)CH2NH2 was alkylated with
     Br(CH2)60CH2CH2Ph to give the analog II.
     araliph amino alc sympathomimetic
KW
IT
     Sympathomimetics
        ((aminomethyl)benzyl alc. derivs.)
IT
     Aminolysis
        (of araliph. bromides)
IT
     Etherification
        (of benzenealkanols)
                123-62-6 94749-45-8
IT
     106-31-0
        (Grignard reaction of, with bromopentane deriv.)
IT
     108-24-7
        (Grignard reactions of)
IT
                 94749-47-0
     24085-19-6
        (alkylation of)
                  36256-45-8 94749-61-8
IT
     27475-14-5
        (amination of)
IT
     94749-00-5
        (aminolysis with, of oxirane deriv.)
IT
               122-97-4 699-02-5 702-23-8
     60-12-8
                                               928-51-8
                                                            1875-88-3
                                        7589-27-7
     3360-41-6
                 5182-44-5
                             5406-18-8
                                                      10493-38-6
                                            52244-70-9 76727-24-7
     10521-91-2
                  22545-13-7
                               30595-80-3
        (etherification of)
IT
                111-24-0
                           4549-31-9
     110-52-1
        (etherification with, of benzenealkanols)
IT
     629-03-8
        (etherification with, of benzenealkenols)
IT
     4549-32-0
        (etherification with, of benzeneethanol)
```

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IT
     94749-46-9P
        (prepn. and alkylation of)
IT
     94749-20-9P
                   94749-21-0P
                                  94749-22-1P
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     94749-25-4P
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                   94749-72-1P
                                  94749-73-2P
     94749-70-9P
        (prepn. and amination of)
IT
     94749-65-2P
        (prepn. and conversion into isocyanate)
IT
     94749-69-6P
        (prepn. and cyclization of)
IT
     94749-48-1P
        (prepn. and deprotection of)
                                 58403-57-9P
                                                94749-41-4P
                                                              94749-42-5P
IT
                  41302-05-0P
     2430-16-2P
        (prepn. and etherification of)
IT
     94749-67-4P
                   94749-71-0P
        (prepn. and hydrogenolysis of)
IT
     94799-94-7P
        (prepn. and methylation of)
IT
     94749-63-0P
        (prepn. and reaction with Et chloroformate)
IT
     94749-66-3P
        (prepn. and reaction with benzyl alc.)
IT
     94749-64-1P
        (prepn. and reaction with sodium azide)
     702-15-8P
                                             94749-50-5P
                                                             94749-51-6P
IT
                 94749-40-3P
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     94749-52-7P
                   94749-53-8P
        (prepn. and reactions of)
IT
     94749-62-9P
        (prepn. and redn. of)
                                                 94749-57-2P
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IT
                   94749-55-0P
                                  94749-56-1P
     94749-54-9P
     94749-59-4P
        (prepn. and reductive alkylation of)
IT
     94749-68-5P
        (prepn. and resolm. of)
                                  94749-43-6P
                                                 94749-44-7P
                                                                94771-31-0P
IT
     94748-99-9P
                   94749-01-6P
     94840-92-3P
        (prepn. of)
IT ·
     94748-69-3P
                   94748-70-6P
                                  94748-71-7P
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                                                               94749-17-4P
     94749-18-5P
                   94749-19-6P
        (prepn. of, as sympathomimetic)
IT
     503-30-0
        (reaction of, with (bromopropyl)benzene)
IT
     637-59-2
        (reaction of, with oxetane)
IT
     32634-68-7
        (resoln. with, of amino ester)
=>
=> d acc 96:163044p all
ANSWER 1
          COPYRIGHT 1992 ACS
AN
     CA96(19):163044p
TI
     Androstane carbothioates
```

CS

Glaxo Group Ltd.

```
PΙ
     NL 8100707 A 16 Sep 1981
ΑI
     NL 81-707 13 Feb 1981
                 15 Feb 1980
PRAI GB 80-5174
     GB 80-13339 23 Apr 1980
     C07J003-00; A61K031-56
IC
SC
     32-4 (Steroids)
DT
     P
CO
     NAXXAN
PY
     1981
LA
     Neth
GI
     Diagram(s) available in offline prints and/or printed CA Issue.
     Antiinflammatory (no data) androstanes I (R = CH2F, CH2Cl, CH2Br,
AB
     CH2CH2F; R1 = acyl; R1R2 = CH2O; R2 = H, .alpha.- or .beta.-Me, R7 =
     H; R2R7 = CH2; R3 = H, C1, F; R4 = H, F; R5 = R6 = H; R5R6 = bond)
     were prepd. Thus, I (R = CH2Cl, R1 = COEt, R2 = .beta.-Me, R3 = F,
     R4 = H, R5R6 = bond, R7 = H) was prepd. by treating the
     corresponding 17-carboxylic acid with Me2NCSCl, hydrolyzing to the
     17-thiocarboxylic acid, and esterifying with BrCH2Cl.
     halomethyl androstanecarbothioate; antiinflammatory halomethyl
KW
     androstanecarbothioate
     Inflammation inhibitors and Antiarthritics
IT
        (halomethyl androstanecarbothioates)
IT
     28416-82-2
                  37927-29-0
        (acylation of)
IT
     53-34-9
               338-95-4
                          2282-51-1
        (oxidn. of)
IT
     80473-87-6P
                   80473-92-3P
                                 80474-39-1P
                                                80486-66-4P
                                                               80486-69-7P
        (prepn. and acylation of)
IT
     80473-82-1P
                   80474-61-9P
                                  80474-66-4P
                                                80474-67-5P
                                                               80474-73-3P
     80474-74-4P
        (prepn. and chlorination of)
IT
     80486-68-6P
        (prepn. and collagen exchange of)
IT
     80473-96-7P
        (prepn. and deacylation of)
IT
     80473-84-3P
        (prepn. and elimination of oxygen from)
IT
     80473-85-4P
                   80473-88-7P
                                 80474-34-6P
                                                80474-38-0P
                                                               80474-43-7P
     80474-45-9P
        (prepn. and esterification of)
IT
                   80483-93-8P
     80474-11-9P
        (prepn. and fluorination of)
IT
                   80474-37-9P
                                  80474-50-6P
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     80474-33-5P
     80474-53-9P
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                   80474-59-5P
     80474-58-4P
                                 80474-60-8P
        (prepn. and hydrolysis of)
IT
     80473-97-8P
        (prepn. and oxidn. of)
IT
     37927-23-4P
        (prepn. and reaction of, with dimethylthiocarbamoyl chloride)
IT
                                  80474-32-4P
     80474-00-6P
                   80474-19-7P
        (prepn. and redn. of)
IT
     79578-10-2P
                   80473-90-1P
        (prepn. and thiolation of)
\mathbf{IT}
     65429-42-7P
                   80473-83-2P
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     80474-46-0P
                   80474-47-1P
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                                                80474-49-3P
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          $0.04 TYMNET
          $0.15 Estimated cost this search
          $0.15 Estimated total session cost 0.003 Hrs.
SYSTEM:OS - DIALOG OneSearch
    File 350:Derwent World Patents Index
                  1963-1980, EQUIVALENTS THRU DW=9151
  **FILE350: KWIC & HILIGHT are available. Format 9 in a full record format
  New predefined format 29 is equivalent to format 3 plus the basic abstract
    File 351:Derwent World Patents Index Latest
                  1981+; DW=9202, UA=9136, UM=9119
  **FILE351: KWIC & HILIGHT are available. Format 9 in a full record format
  New predefined format 29 is equivalent to format 3 plus the basic abstract
            Set
                      Items Description
                     ____
?s pn=gb2088877
                      1 PN=GB2088877
            S1
?t1/3
  1/7/1 (Item 1 from file: 351)
003207407 WPI Acc No: 81-67960D/38
XRAM Acc No: C81-D67960
     Haloalkyl androstane-17-carbothioate ester(s) useful as topical
     antiinflammatory agents
Patent Assignee: (GLAX ) GLAXO GROUP LTD
Number of Patents: 030
Patent Family:

        CC Number
        Kind
        Date
        Week

        BE 887518
        A
        810813
        8138

        SE 8101010
        A
        810914
        8140

        FR 2477156
        A
        810904
        8141

        NL 8100707
        A
        810916
        8142

        FI 8100444
        A
        810930
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        PT 72502
        A
        811012
        8144

        DK 8100623
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        811028
        8149

        DE 3105307
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        811210
        8151

        FR 2485542
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        811231
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        GB 2088877
        A
        820616
        8224

        US 4335121
        A
        820615
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        ZA 8100976
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        820519
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        ES 8305379
        A
        830701
        8334

        GB 2088877
        B
        840704
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        ES 8402317
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        840815
        8438

        GB 2137206
        B
        850403
        8514

        ES 8502447
        A
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        8524

        CH 651307<
                                  Kind Date
        CC Number
                                                                         Week
                                                810813
        BE 887518
                                 A
                                                                         8138
                                                                                       (Basic)
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8833

Priority Data (CC, No, Date): GB 8013339 (800423); GB 805174 (800215); GE 814496 (810213); GB 8325400 (830000);

Applications (CC, No, Date): GB 8325400 (830922); US 513396 (830714); ES 532055 (840430); DE 3153379 (810213); US 753428 (850710); JP 8120790 (810213); DE 3105307 (810213);

Filing Details: GB2137206 Derived from 13.02.81-004496; US4578221 (+23.4.81, 17.8.82-US-256845, 408837) (1665SE); DE3153379 Div.ex.3105107; US4650610 C.i.p 4578221 (+23.4.81, 17.8.82, 14.7.83-US-256845, 408837, 513396) (1665CJ); DE3105307 Add to 3153379 (1822JS)

Abstract (Basic): Carbothioate esters of formula (I) are new. In (I) R1 isCH2F, CH2Cl, CH2Br or CH2CH2F; R2 is 2-4C alkanoyl or OR2 + R3 is 16 alpha, 17 alpha-isopropylidenedioxy; R3 is H, alpha- or beta-Me or =CH2; R4 is H, Cl or F; R5 is H or F. Intermediates of formula (II) and their salts are new. In (II) Ra is COOCSNRARB or COSR1A, where RA and RB are alkyl or NRARB is a 5- to 8-membered ring opt. contg. another heteroatom (O, N or S) and opt. mono- or disubstd. by 1-3C alkyl, and R1A is H, R1 or a gp. convertible to R1; Rb is esterified OH or forms an isopropylidenedioxy gp. with Rc or Rb can be OH when Ra is COSR1A; Rc is H, Me or =CH2; Rd is opt. protected OH or oxo and Re is H, Br, Cl or F, or Re + Rd is a C-C bond or a beta-epoxy gp.; Rf is H or F.

(I) are antiinflammatory agents with a high ratio of topical to systemic activity. (74pp)

Abstract (US): 8713 US 4650610

Androstane and carbothioic acids and salts of formula (I) are new. In (I), R1 is H, OH in alpha configuration, Me in alpha or beta-configuration or methylene; R2 is OH opt. protected (alpha or beta) or oxo; R3 is H, Br, Cl, F or R2 and R3 together are C-C bond or epoxy gp. in beta-configuration; R4 is H or F. Esp. cpds. include 9alpha-fluoro-11beta 17alpha-dihydroxy -16beta-methyl--3-oxoandastra-1,4-diene 17beta-carbothioic acid. (I) may be prepd. e.g. by reacting a reactive deriv. of 17beta-carboxylic acid (II) pref. (III)), with H2S or sulphide or hydrosulphide.

USE - (I) are intermediates to corresp. 17beta-carbothioate esters by esterification and to the 17alphaacyloxy and 16alpha 17alpha-acetonide cpds. which are anti-inflammatories. @(9pp)@ 8615 US 4578221

Androstane hydroxy carbothioic acids and salts of formula (I) are new. In (I), R1 is H, OH in alpha configuration, Me in either alpha or beta or methylene; R2 is opt. protected in either alpha or beta configuration or methylene; R3 is H, Br, Cl, F or R2 and R3 together are C-C bond or epoxy in beta configuration; R4 is H or F and dotted line is single or double bond.

(I) is prepd. by reacting reactive deriv. of corresp. 17-beta-carboxylic acid cpd. (III) with H2S, sulphide or hydrosulphide salt. In (III), R5 is gp(a) with X, Y and Z each CH or N2 one or two being N, the ring opt. substd. lower alkyl or Bz. (III) is pref. prepd. by reaction of reactive deriv. of corresp. 17-beta-carboxylic acid (II) with R5-W-R5 in which W is CO, CS, SO or SO2 (pref. N, N'-carbonyldimidazole or N-N'-thiocarbonyl-dimidazole). New process for prepn. of cpd. (V) in which Ra is 1-6C alkyl or 1-2C alkyl with terminal halo or Bz opt. substd. 1-4C-alkyl or -alkoxy or halo comprises esterifying (I) or its salt.

USE - (I) are intermediates to anti-inflammatory androstane 17-beta-carbothicate esters. The process allows prepn. of the 17-beta-carbothicate esters when corresp. thicks are not available. @(9pp)@

Abstract (GB): 8514 GB 2137206

Compounds of the general formula (II) (wherein Ra represents a thiocarbamoyloxycarbonyl group -COOCSNRARB (where RA and RB which may be the same or different, are alkyl groups or RA and RB together with the nitrogen atom to which they are attached form a 5-8 membered ring which may optionally contain an additional hetero atom selected from oxygen, nitrogen and sulphur and/or which may be optionally substituted

for R1 or is the group -(CH2)nY in which n is 1 or 2 and Y represents a displaceable substituent) and Rb represents an esterified hydroxyl group or Rb and Rc together represent an isopropylidenedioxy group; or where Ra represents a group COSR(1A), Rb is optionally a hydroxyl group; Rc represents a hydrogen atom, a methyl group (which may be in either the alpha- or beta-configuration) or a methylene group; Rd represents a hydroxy or protected hydroxy group (in either the alphaor beta-configuration) or an oxo group; Re represents a hydrogen, bromine, chlorine or fluorine atom; or Rd and Re together represent a carbon-carbon bond or an epoxy group in the beta-configuration; Rf represents a hydrogen or a fluorine atom; and salts of those compounds which have a free carbothioic acid group; with the exclusion of compounds of the formula (I) wherein R1 represents a fluoro-, chloroor bromo- methyl group or a 2'-fluoroethyl group, R2 represents a group COR6 where R6 is a C1-3 alkyl group or OR2 and R3 together form a 16alpha,17alpha isopropylidenedioxy group; R3 represents a hydrogen atom, a methyl group (which may be in either the alpha- or beta-configuration) or a methylene group; R4 represents a hydrogen, chlorine or fluorine atom; R5 represents a hydrogen or fluorine atom. 8427 GB 2088877

Cpds. of the formula (I) wherein R1 represents a fluoro-, chloroor bromo-methyl gp. or a 2'-fluoroethyl gp., R2 represents a gp. COR6
where R6 is a C1-3 alkyl gp. or OR2 and R3 together form a
16alpha,17alpha isopropylidenedioxy gp.; R3 represents a hydrogen atom,
a methyl group (which may be in either the alpha- or betaconfiguration) or a methylene gp.; R4 represents a hydrogen, chlorine
or fluorine atom; R5 represents a hydrogen or fluorine atom and the
dotted line represents a single or double bond.

Abstract (DE): 8839 DE 3105307

Androstan-carbothioate of formula (I) is new, where R1 = F, C1, Br or 2'-fluoroethyl. R2 = COR6 (R6 = 1-3C alkyl); or OR2 and R3 form 16 alpha, 17 alpha-isopropylidene dioxy together R3 = H, alpha- or beta-methyl or methylene. R4 = H, Cl or F. R5 = H or F and dotted lines (I) within benzyl denote single or double bond.

5 cpds. are specifically claimed including S-Chloromethyl-9alpha -fluoro-11 beta-hydroxy-16 alpha-methyl-3-oxo-17 alpha propionyloxy androsta-1,4-dien-17 beta carbothioate.

6 methods of preparing (I) are claimed including reducing a cpd. of (I) which bears 11-oxo gp.

USE/ADVANTAGE - (I) is antiinflammatory steroids. @(26pp)@Derwent Class: B01;

Derwent Registry Numbers: 0361-S; 0442-S; 1685-S; 1722-S

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PN=GB2140800
      S2
?t2/7
 2/7/1
           (Item 1 from file: 351)
004119333
           WPI Acc No: 84-264874/43
XRAM Acc No: C84-112012
   New 1-phenyl-2-amino-1-ethanol derivs. useful as beta-2 adrenergic
    stimulants
Patent Assignee: (GLAX ) GLAXO GROUP LTD
Author (inventor): SKIDMORE I F; LUNTS L H C; FINCH H; NAYLOR A
Number of Patents: 030
Patent Family:
    CC Number
                 Kind
                          Date
                                     Week
    DE 3414752
                   Α
                          841018
                                     8443
                                            (Basic)
    BE 899448
                   Α
                          841018
                                     8444
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Applications (CC, No, Date): DE 3414752 (840418);
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029568) (367MW); US4992474 (1665SV) (+19.11.86-US-932359; 23.6.83,

4.11.83-GB-317087, 329568)

of formula (I) and their salts and solvates are new. In(I) m=2-8 and n=1-7, provided that m+n=4-12; Ar=phenyl opt. substd. by 1 or 2 of halogen, 1-3C alkyl and 1-3C alkoxy or by O(CH2)pO, where p=1 or 2; RI and R2 = H or 1-3C alkyl, provided that the total no. of C atoms in R1 and R2 is not more than 4.

USE - (I) are beta-2 adrenergic stimulants useful for treating asthma, chronic bronchitis, premature labour, depression, congestive heart disease, inflammatory and allergic skin disorders, psoriasis, glaucoma and peptic ulcers. @(82pp Dwg.No.0/0)@

Abstract (US): 9109 US 4992474

4-Hydroxy-alpha -(((6-(4-phenylbutoxy)(and corresp. propoxy cpd.) hexyl)amino) methyl)-1,3-benzenedimethanol and its 1-hydroxy-2-naphthalene carboxylate, salts and solvates, are new.

It may be prepd. e.g. by alkylation of corresp. amine.

USE - Selective stimulation of beta2-adrenoreceptors in treatment of asthma, bronchitis, etc. @(24pp)@

Abstract (GB): 8801 GB 2176476

Compounds of the general formula (II): wherein m is an integer from 2 to 8 and n is an integer from 1 to 7 with the proviso that the sum total of m+n is 4 to 12; Ar represents a phenyl group which may be unsubstituted or substituted by one or two substituents selected from halogen atoms, E1-3 alkyl and C1-3 alkoxy groups, or by an alkylenedioxy group of formula -O(CH2)pO- where p is 1 or 2; R1 and R2, which may be the same or different, each represents a hydrogen atom or a C1-3 alkyl group with the proviso that the sum total of carbon atoms in R1 and R2 is not more than 4; and Y1 is a hydrogen atom or a group convertible thereto by catalytic hydrogenation; and acid addition salts thereof. 8738 GB 2140800

Compounds of the general formula (I): wherein m is an integer from 2 to 8 and n is an integer from 1 to 7 with the proviso that the sum total of m+n is 4 to 12; Ar represents a phenyl group which may be unsubstituted or substituted by one or two substituents selected from halogen atoms, C1-3 alkyl and C1-3 alkoxy groups, or by an alkylenedioxy group of formula -O(CH2)pO- where p is 1 or 2; and R1 and R2, which may be the same or different, each represents a hydrogen atom or a C1-3 alkyl group with the proviso that the sum total of carbon atoms in R1 and R2 is not more than 4; and physiologically acceptable salts and solvates thereof.

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Derwent Class: B05;
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Int Pat Class: A61K-031/13; C07C-093/08; C07D-317/54; C07D-319/18;
    A61K-000/00; C07C-000/00; C07C-033/20; C07C-043/02; C07C-047/27;
    C07C-049/25; C07C-059/58; C07C-097/10; C07C-103/30; C07D-031/92;
    C07D-325/00; C07C-039/11; C07C-087/00; C07C-091/30; C07C-125/06;
    C07C-143/68; C07C-039/12; C07C-023/00; A01K-031/13; C07D-307/48;
    C07C-087/28; C07C-217/10; C07C-213/02; C07C-215/00

Derwent Registry Numbers: 0199-S; 0329-S; 0882-S; 1067-S; 1069-S; 1714-S
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S2	1	PN=GB2140800
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